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Microwave heating behavior and microwave absorption properties of barium titanate at high temperatures

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The temperature dependence of the microwave absorption behavior of $BaTiO_3$ particles was investigated over various frequencies and temperatures of 25-1000 °C. First, using both the coaxial transmission line method and the cavity perturbation method by a network analyzer, the real and imaginary parts of the relative permittivity of $BaTiO_3$ (ε_r' and ε_r'', respectively) were measured, in order to improve the reliability of the data obtained at 2.45 GHz. The imaginary parts of the relative permittivity as measured by the two methods were explored by their heating behaviors. Furthermore, the temperature dependence of the microwave absorption behavior of $BaTiO_3$ particles was investigated for frequencies of 2.0-13.5 GHz and temperatures of 25-1000 °C using the coaxial transmission line method.
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I. INTRODUCTION

Of late, microwave-based heating is being explored for use for both the synthesis and sintering of barium titanate, which is of interest owing to its high dielectric constant and ferroelectric properties. Jida *et al*. investigated the microstructure and electrical properties of $BaTi_{1-x}Nb_xO_3$ ceramics prepared by microwave sintering at temperatures of 1300-1400 °C. They reported that the use of the microwave sintering technique and a dopant that forms donor levels even at high doping levels results in high-performance ceramics with a positive temperature coefficient of resistivity.[1] Ma *et al*. synthesized tetragonal $BaTiO_3$ at 170 °C by both microwave heating and conventional heating followed by sintering at 850 °C for 2-4 h. They claimed that a metastable cubic phase crystallized much faster in the sample synthesized by microwave heating than in the one formed by conventional heating.[2] Malghe *et al*. reported that $BaTiO_3$ in the cubic form could be synthesized from $BaTiO(C_2O_4)_2E4H_2O$ (BTO) at temperatures as low as 500 °C. They claimed that the thermal decomposition of BTO presumably yields hypo-stoichiometric TiO_2 by virtue of the presence of CO that evolves during the reaction, which, in the presence of the microwave field, combines with BaO to yield the cubic phase. As a result, the cubic $BaTiO_3$ transforms completely into the tetragonal form on heating in a microwave field at temperatures higher than 700 °C.[3] These studies employed microwaves as a new heating source, since they exhibit numerous advantages over conventional methods such as allowing for rapid and selective heating. When material processing is done using microwaves as the energy source, their frequency can be varied to control the amount of energy delivered. Nyutu *et al*. synthesized nanocrystalline tetragonal barium titanate ($BaTiO_3$) with particle sizes of 30-100 nm. They employed microwaves with frequencies of 3-5.5 GHz and different bandwidth sweep times and compared the effects of the microwave frequency, microwave bandwidth

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sweep time, and aging time on the microstructure, particle size, phase purity, surface area, and porosity of the obtained $BaTiO_3$ sample.[4]

The temperature dependence of the microwave absorption properties of $BaTiO_3$ particles requires further investigation, if one wishes to elucidate the chemical mechanisms underlying each of the processes involved in the synthesis. Determining the microscopic thermal distribution is a reasonable way to account for the advantages of these processes. Microwaves heat different materials differently, based on their absorption properties; this results in an inhomogeneous thermal distribution on the micron scale. Such thermal distributions may result in anomalous chemical behaviors, which have been observed previously during the chemical synthesis of ceramics from powdery mixtures. However, the validity of the measured absorption properties, which determine the thermal distribution in the case of powdery materials, is unknown for high temperatures. (The issue of the absorption properties of powdery materials at high temperatures is discussed in a later section.)

In the present study, the temperature dependence of the microwave absorption properties of $BaTiO_3$ powders was experimentally investigated at frequencies of 2.0-13.5 GHz and temperatures of 25-1000 °C. We first investigated the relative permittivity at a frequency of 2.45 GHz, using both the cavity perturbation method and the coaxial transmission line method. Next, the $BaTiO_3$ powders were heated using microwaves and their permittivities were examined through thermal analyses. Finally, the temperature dependence of the microwave absorption properties of the $BaTiO_3$ powders was estimated for frequencies of 2.0-13.5 GHz and temperatures of 25-1000 °C.

II. EXPERIMENTAL PROCEDURE

We used the cavity perturbation method[5,6] to determine the relative permittivity of $BaTiO_3$ particles (BT-04, Sakai Chemical Industry) as a function of the temperature. This method is advantageous for high-temperature measurements because it does not require that the test apparatus be attached to the sample, when it is being heated to high temperatures. The measurement system used consisted of a cylindrical cavity, pipes for dry air and liquid antifreeze for temperature control, and a network analyzer, as shown in Fig. 1. The silica tube had little effect on the microwave distribution

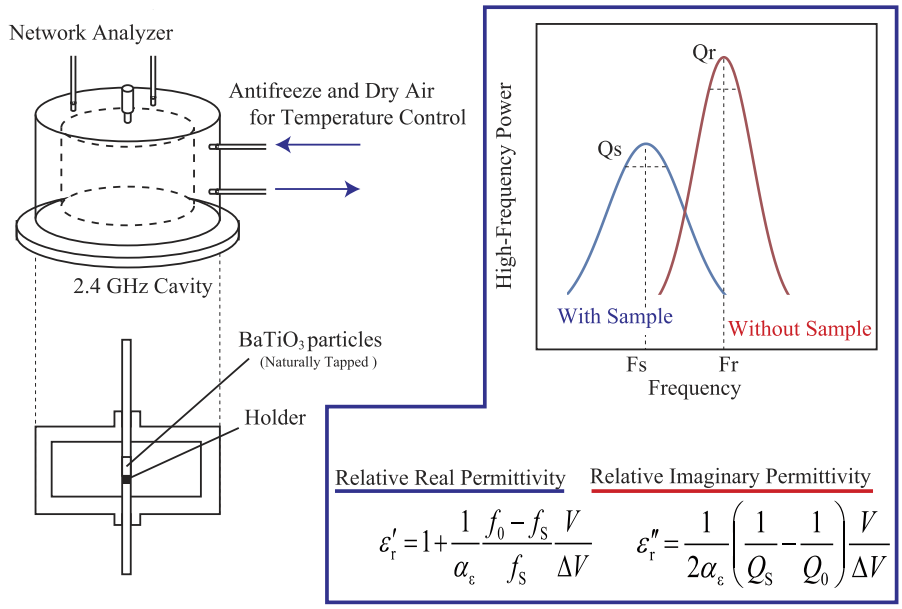

FIG. 1. Schematic illustration of the cavity perturbation method, where ε'_r is the relative real permittivity, ε''_r is the relative imaginary permittivity, Q_r is the Q factor of the blank cavity, Q_s is the Q factor of the sample-charged cavity, f_r is the resonance frequency of the blank cavity, f_s is the resonance frequency of the sample-charged cavity, Δf is the half-power bandwidth, V is the volume, and ΔV is the sample volume. Further, α is perturbation coefficient (=1.855 in this study) and employed frequency is 2.4 GHz in this measurement.

and was therefore used as a sample holder. The samples were fixed with a Teflon susceptor at the centre of the cavity. The samples (19.845 mm^3) were maintained at the predetermined temperatures (-100 to 100 °C) by making both dry air and liquid antifreeze flow into the cavity. The Q factor and resonance frequency of the cavity changed depending on the material properties of the sample being tested. The network analyzer monitored the Q factor and resonance frequency of the system, and ε_r' and ε_r'' were calculated based on these values (refer to Fig. 1). The cavity exhibited the TM_{010} mode (in the TM mode, the Poynting vectors of the electromagnetic field are vertically controlled by the magnetic field), and a perturbation coefficient (α) of 1.855 was employed.

Using the coaxial transmission line method, the real and imaginary parts of the relative permittivity (i.e., ε_r' and ε_r'', respectively) were measured for temperatures of 25-1200 °C and microwave frequencies of 2.0-13.5 GHz. A network analyzer (Agilent Technologies, N5230A), coaxial cables, and an APC7 coaxial sample holder (See Refs. 7 and 8) were employed for the purpose. The sample holder was made of SUS316L stainless steel and was 300 mm long. The temperature was increased at a rate of 10 °C/min during the measurements using an electric resistance furnace. The transmission and reflection values (i.e., the S parameters) of the microwave radiation were measured approximately every 50 °C during the heating cycle. The network analyzer had an output power of approximately 1 mW. Each measurement was performed over frequencies of 2.0-13.5 GHz and required approximately 2 s. The complex permittivity and permeability were calculated from the S parameters using a method developed by the National Institute of Standards and Technology.[9] To calculate the complex permittivity and permeability at high temperatures, air was used as the reference. Thermocouples were attached to the outside of the sample holder to counter the effects of diffraction by the metal wires. The actual temperatures of the $BaTiO_3$ powders were estimated from preliminary experiments. The temperatures were measured with a thermocouple attached to the outer wall of the sample holder instead of being placed in the sample.

During the preliminary experiments, the apparent and true temperatures were measured during the heating cycle using a thermocouple attached to the outer wall of the holder and one embedded in the sample. When Thermocouples exists in the cavity, it disturbs electromagnetic field in the coaxial line. To remove the problem, we measured outside temperature the apparent temperature) to estimate inside temperature (true temperature). The apparent temperature (T_{app}) varied almost linearly with the true temperature (T_{true}) as per the following expression, $T_{app} = T_{true} \times 1.0313 + 43.237$ °C, which was used to correct the data. The measured temperatures were thus the apparent temperatures and were corrected to obtain the true temperatures. In this manner, the actual temperatures of the $BaTiO_3$ particles could be determined from the apparent temperatures, monitored by outside of waveguides.

As mentioned previously, we examined the microwave heating behavior of $BaTiO_3$ particles, in order to elucidate their absorption properties. For the heating experiments, an applicator with a 2.45 GHz semiconductor oscillator, an isolator, WRJ-2 waveguides, an iris, and a plunger (See Ref. 10) were employed. The semiconductor oscillator could generate microwaves with a frequency of 2.45 GHz at a total output power of 500 W. The microwaves were focused by the iris, resulting in a TE_{103} wave in the cavity. The iris had a 28 mm slit that was parallel to the direction of the electric field. The plunger was placed at the end of the waveguide. This system allowed us to spatially separate the electric and magnetic fields of the microwaves. The sample being tested was placed at an electric-field node (denoted by E_{max}, where the magnetic field is zero). The temperature of the reactants was monitored using a radiation thermometer. The powers of the incident and reflected microwaves were also monitored.

III. RESULTS AND DISCUSSIONS

The relative permittivity (ε_r' and ε_r'') of the $BaTiO_3$ (BT04) particles was indicative of a complex behavior. Figure 2 shows the temperature dependence of the relative complex permittivity (ε_r'') for the $BaTiO_3$ powders at temperatures of -50 to 200 °C as determined using (a) the coaxial transmission method (shown as C. T. L. in the figure) and (b) the cavity perturbation method (shown as C. P. M. in the figure) at 2.4 GHz microwave frequency. The complex permittivity increased with the temperature for temperatures higher than 0 °C, as can be seen from the C. P. M results. This

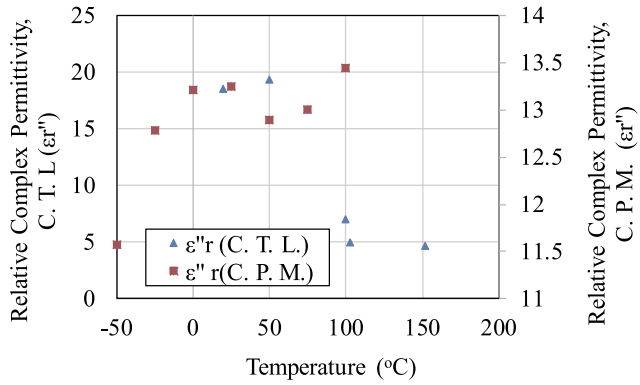

FIG. 2. Temperature dependence of the relative complex permittivity (ε_r'') of $BaTiO_3$ powder at the temperatures of -50 to 200 °C determined using (a) the coaxial transmission method (shown as C. T. L. in this figure) and (b) the cavity perturbation method (shown as C. P. M. in this figure) at 2.4 GHz microwave frequency. The C. T. M. relative complex permittivity values were lower than the C. P. M. values.

increase is thought to be related to the orthorhombic-to-tetragonal transition of $BaTiO_3$. At the Curie temperature of $BaTiO_3$ (100 °C), the complex permittivity decreased, as can be seen from the C. T. L results. The results of C. T. L were considered reasonable because changing of the permittivity with their transition were observed.

It can be seen that the C. T. L. complex permittivity values were different from the C. P. M. values. Even though the powder samples should have similar complex permittivities at temperatures of 0-100 °C, the measured values were not similar. It is well known that these methods sometimes result in different values, which would explain the differences observed in the present study.

Microwave heating behavior were investigated to discuss absorption properties of $BaTiO_3$. The C. T. L. permittivity values were more indicative of the microwave heating behavior than were the C. P. M. values considering their heating behavior. Figure 3 shows the temperature versus time plots of the $BaTiO_3$ particles at E_{max}. At point D, the heating behavior curve exhibits an inflection point; this was the hot spot corresponding to microwave heating. According to the steady-state theory of energy conservation during microwave heating, the amount of power delivered to the $BaTiO_3$ powder compact per unit volume is given by

$$w_{in}(T) = \frac{1}{2}(\omega\epsilon''(T) \mid E \mid^2 + \omega\mu''(T) \mid H \mid^2) \tag{1}$$

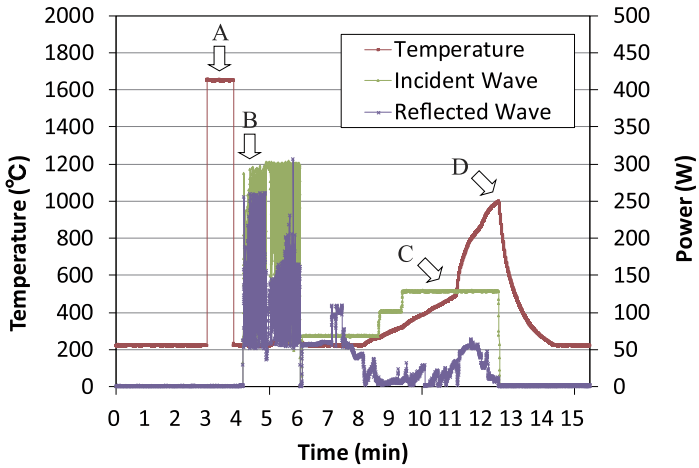

FIG. 3. Time vs. temperature plots of the $BaTiO_3$ powder at E_{max}. When the laser pointer was on, the measured temperature was the maximum, as denoted by the letter A in this figure. When the microwaves were irradiated, the temperature of the sample particles increased steeply (B) and then increased less rapidly at a constant incident wave power (C). At point D, the microwaves were turned off and the temperature decreased accordingly.

where $w_{in}(T)$ is the input power per unit volume at the observation point (note that another form of Eq. (1) includes the energy transition induced by the current; in this paper, we employed the form shown above). In the case of $BaTiO_3$, the second term in Eq. (1) is negligibly small, so that $w_{in}(T)$ is proportional to $\epsilon''(T)$. In contrast, the energy transmitted to the substrate from the $BaTiO_3$ powder compact is given by

$$w_{out}(T) = \alpha \bigtriangledown T + \int C_p(T)dT + \theta\delta T^4 \tag{2}$$

where α is the heat-transfer coefficient, δ is the product of the Stefan-Boltzmann constant and the emissivity ($= 5.67 \times 10^{-8} W m^{-2} K^{-4}$), and θ is the emissivity. At point C, the input power should be equal to the output power for cold powders.[11] Further, this point is determined by the absorption properties of the materials in question and the energy transmitted to the substrate from the powder as follows:

$$\epsilon_r''(T) = \frac{2\theta\delta T^4}{\epsilon_0 \omega E^2} \frac{S}{V} \tag{3}$$

Using Eq. (3), ϵ_r'' was estimated to be 4 (where V = 8 $\times 10^{-6}$ m^3, S = 2.4 $\times 10^{-4}$ m^2, θ = 0.8, δ = 5.67 $\times 10^{-8}$ W m^2 K^{-4}, and T = 450 °C). Further, E was estimated to be 5 $\times 10^3$ V m^{-1} through a simulation that employed the same iris (slit width of 28 mm).[12] The estimated value for ϵ_r'' agreed well with the value determined experimentally by C. T. L (the values determined using the two methods were similar; however, the C. T. L. complex permittivity values were slightly higher than the C. P. M. values at temperatures of 0-100 °C).[13]

The real part of the permittivity decreased with the microwave frequency at temperatures of 700 °C and lower but increased at temperatures of 700-900 °C. Further, the imaginary part of the permittivity and the loss factor increased with the temperature, as shown in Fig. 4. Considering the phase diagram of barium titanate ceramics,[14] these ceramics do not exhibit a phase transition at 700 °C. This is because the electrical conductivities related to electrons and holes increase at high temperatures. In $BaTiO_3$, the major electronic carriers are electrons and holes. These charge carriers depend on the defect types, which, in turn, depend on the dopants used as well as the temperature and oxygen partial pressure. The permittivity of $BaTiO_3$ powders can be determined using $\epsilon'' \approx (\sigma_e + \sigma_h/\omega)i$, where σ_e and σ_h are the static electrical conductivities because of electrons and holes respectively, and ω is the angular frequency. In the present study, ϵ_r'' increased exponentially with the temperature; this was in keeping with what one would expect in the case of microwave absorption by metal oxides.

Another phenomenon can be seen in the figure (see Fig, 4(c)). The loss factor versus frequency curve exhibited two maxima (frequencies of 2-6 and 8-11 GHz) at temperatures of 1000 °C and higher. The increase in the loss factor was owing to the sample length microwave frequency resonance

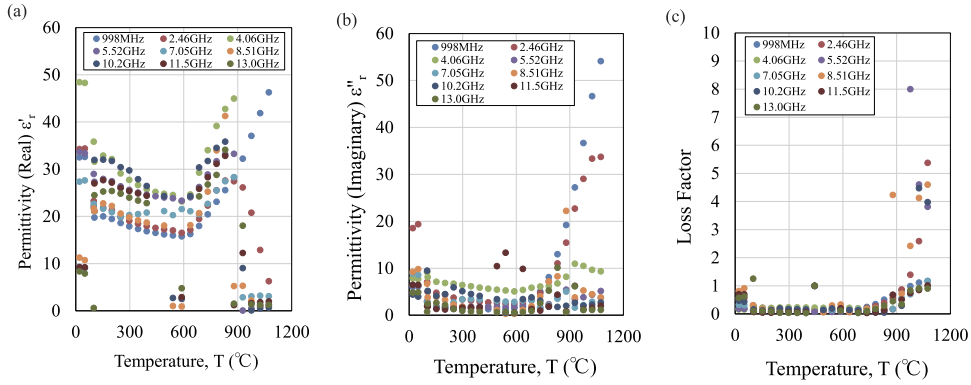

FIG. 4. Temperature dependence of the relative complex permittivity ((a) ε_r' and (b) ε_r'') of $BaTiO_3$ powder (particle size of 6.3 $\times 10^{-1}$ μm; filling rate of 63 %) at various frequencies. At 2.45 GHz, the value of ε_r'' changed at the phase-transition temperature of $BaTiO_3$ (100 °C). Further, ε_r' r was negatively correlated to the microwave frequency at temperatures of 879 °C and higher. (c) The loss factor and ε_r'' increased significantly at temperatures of 900 °C and higher.

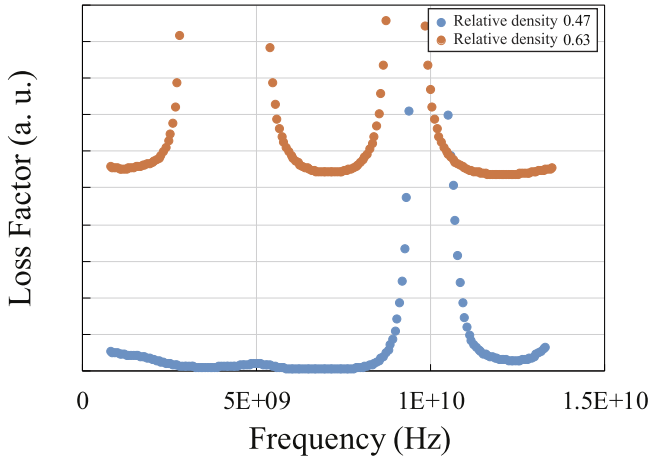

FIG. 5. Loss factor as a function of the frequency for $BaTiO_3$ powder (particle size of 6.3 $\times 10^{-1}$ μm) filling rates 63 % and 47 %. Absorption resonance was observed at both filling rates.

at the frequencies of 2-6 GHz, considering that the peak disappeared as the relative density was changed from 0.63 to 0.49. The peak at 8-11 GHz was probably related to polaritons. At high temperatures, the individual particles of a material that exhibits high microwave absorbance exhibit anomalous absorption behaviors, which depend on their morphology.[15,16] Even though sintering was performed in the study, the radii of the particles after sintering were almost similar to those before sintering.[13] Therefore, the observed behavior can be attributed to the individual particles of the barium titanate ceramics, since the peak was observed at different relative densities (see Fig. 5 and Ref. 13).

IV. SUMMARY

The temperature dependence of the microwave absorption behavior of $BaTiO_3$ particles was investigated for various frequencies and temperatures of 25-1000 °C. Using both the coaxial transmission line method and the cavity perturbation method, which involved the use of a network analyzer, the real and imaginary parts of the relative permittivity (ε_r' and ε_r'', respectively) were measured, in order to improve the reliability of the data obtained at 2.45 GHz. It was found that the two methods resulted in similar values at temperatures of 0-100 °C. However, the values were different at temperatures higher than 100 °C. To determine whether the obtained values were valid, the microwave heating behavior was investigated, since the heating behavior of $BaTiO_3$ particles is determined by their microwave absorption properties. Furthermore, the temperature dependence of the microwave absorption behavior of $BaTiO_3$ particles was investigated for frequencies of 2.0-13.5 GHz and temperatures of 25-1000 °C using the coaxial transmission line method. The imaginary part of the permittivity was well described by the electrical conductivity. Further, an anomalous behavior was observed in the loss factor curve.

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[13] See supplementary material at http://dx.doi.org/10.1063/1.4953325 for particle size distribution before and after laser scattering, and X-ray diffraction spectra of BT4 before and after the measurements. We should emphasize that this estimation includes an error bar from decision of strength of electrical field (E [V/m]). The electrical field around sample powders were sensitive to microwave oscillator, sample states, slit width and adjustments of cavity. $E = 5 \times 10^3$ V m^{-1} are thought to be reasonable considering the results of simulation but the simulation can not follow both the adjustment of cavity and sample states. Third method of electrical permittivity at high temperature need to be developed for decision of the validity of measurements.
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